

Title	Studies on the Catalytic Action of Basic Catalysts : Factors Governing the Aldol Condensation of Crotonaldehyde
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Table 2. Mechanical properties at the elevated temperature.

Materials	Temp. (°C)	10	50	100	150	200	220	230
Ordinary Vinylon	Tenacity (g)	5.26	5.46	4.63	3.00	1.51	0.82	0.75
	Elong. (%)	20.8	29.1	37.2	39.7	50.9	36.8	33.1
	Young's Modulus (Kg/mm ²)	496	349	288	91	25	20	20
Vinylon AN	Tenacity	6.09	5.60	5.00	3.35	2.14	1.71	1.71
	Elong.	25.3	28.2	29.3	30.6	26.1	22.3	23.7
	Young's Modulus	524	266	200	42	21	22	20

25. Studies on the Catalytic Action of Basic Catalysts : Factors Governing the Aldol Condensation of Crotonaldehyde

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As R. Kuhn (Ber., 68, 98 (1936)) and S. Hunning (Ann. 569, 198 (1950)) have shown, the aldol condensation of crotonaldehyde takes place only in the simultaneous presence of acid and base, especially when organic nitrogen bases such as piperidine are used as basic catalysts. In reference to this conjugative action of the acid and base catalysts, we have investigated the effect of the natures of acids and bases in combination, the mol ratio of acid to base, the amount and concentration of the catalyst, the reaction temperature, and the solvent upon the reaction.

The extent of the condensation was determined by the removal of the unreacted crotonaldehyde by fractional distillation.

The catalytic activity of the acetate of the cyclic secondary amines such as piperidine or pipercoline (α) was found to be by far larger than that of the corresponding tertiary amines, pyridine or picoline (α), or that of the ordinary alkali hydroxides.

A molecular proportion of the acid and the base, i.e. acetic acid and piperidine, was satisfactory for the condensation, and an excess of the acid or the base around this mol ratio showed but little effect on the extent of the reaction.

As for the natures of the acid used as catalyst in conjunction with piperidine and pyridine as the basic component it was shown that an acid with a pK value of 3 to 5 is preferable as the acid component of the catalyst. Stronger or weaker acids were found to be quite unsatisfactory in this connection.

The rate of condensation increased exponentially with the increase in the catalyst concentration and, naturally, with temperature.

Alcoholic solvents had no appreciable influence upon the reaction rate in comparison with that of the homogeneous, solvent less, reaction. A retarding action of water was observed in the case of the methanol solvent but in butanol as solvent the effect was hardly observable.

The condensation product was analyzed by the hydrogenation in the presence of nickel catalyst at 120°C. under a hydrogen pressure of about 100 atm., followed by fractional distillation. It was found that the content of the higher condensates containing more than twelve carbon atoms in the molecule and the condensates of the cyclic nature in the product increased with the catalyst concentration, the mol ratio of the catalyst to the crotonaldehyde used, and the reaction temperature.

26. Studies on the Reaction between Ammonia and Carbon Disulfide at High Pressures. (I)

Influences of the Charging Quantity of NH_3 and CS_2 , and their Mol Ratio on the Formation of Ammonium Thiocyanate

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The reaction of ammonia with carbon disulfide giving NH_4SCN was studied in an autoclave at 110° C. changing the reaction times. After the autoclave was heated in an oil bath for a definite time, it was cooled quickly bringing into a bath cooled with running water and allowed to stand over night continuing to cool with water and then the pressure was released in cold state, the products were dissolved in methanol, and NH_4SCN in the products was determined with N/10 AgNO_3 solution.

In a case where the mol ratio of NH_3 to CS_2 is 2:1, the yield of NH_4SCN is decreased, as the charging density of NH_3 and CS_2 is increased. When the mol ratio of NH_3 to CS_2 is 4:1, the yield of NH_4SCN is independent on the charging density, and amounted to 90%. As the mol ratio of NH_3 to CS_2 is increased, the formation of NH_4SCN is increased. Released the pressure in the autoclave at a hot state immediately after the reaction has ended, a remarkable decrease in the yield of NH_4SCN is observed.

The results may be interpreted as follows. In the autoclave the following reactions exist in a state of an equilibrium.